AGU PUBLICATIONS

Global Biogeochemical Cycles

RESEARCH ARTICLE
10.1002/2016GB005498

Key Points:
- Legacy nitrogen contributes 85% of annual nitrate-N loads in the Mississippi River Basin and 47% in the Susquehanna River Basin
- Nitrate-N has accumulated in groundwater aquifers on the order of 500-1000 kg ha in the two study watersheds
- Our results indicate a strong hysteresis effect, with changes in annual N loads lagging behind decreases in annual N surplus values

Supporting Information:
- Supporting Information S1

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Citation:
Van Meter, K. J., N. B. Basu, and P. Van Cappellen (2017), Two centuries of nitrogen dynamics: Legacy sources and sinks in the Mississippi and Susquehanna River Basins, *Global Biogeochem. Cycles*, *31*, 2–23, doi:10.1002/2016GB005498.

Received 8 AUG 2016
Accepted 22 NOV 2016
Accepted article online 1 DEC 2016
Published online 7 JAN 2017

Two centuries of nitrogen dynamics: Legacy sources and sinks in the Mississippi and Susquehanna River Basins

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Abstract Global flows of reactive nitrogen (N) have increased significantly over the last century in response to agricultural intensification and elevated levels of atmospheric deposition. Despite widespread implementation conservation measures, N concentrations in surface waters are often remaining steady or continuing to increase. Although such lack of response has been attributed to time lags associated with legacy N stores in subsurface reservoirs, it is unclear what the magnitudes of such stores are and how they are partitioned between shallow soil and deeper groundwater reservoirs. Here we have synthesized data to develop a 214 year (1800–2014) trajectory of N inputs to the land surface of the continental U.S. We have concurrently developed a parsimonious, process-based model, Exploration of Long-tErM Nutrient Trajectories (ELEMeNT) that pairs this input trajectory with a travel time-based approach to simulate transport and retention along subsurface pathways. Using the model, we have reconstructed historic nitrate yields at the outlets of two major U.S. watersheds, the Mississippi River Basin (MRB) and Susquehanna River Basin (SRB). Our results show significant N loading above baseline levels in both watersheds before the widespread use of commercial N fertilizers, largely due to the conversion of forest and grassland to row crop agriculture. Model results also allow us to quantify the magnitudes of legacy N in soil and groundwater pools and to highlight the dominance of soil legacies in MRB and groundwater legacies in SRB. Approximately 55% and 18% of the current annual N loads in the MRB and SRB were found to be older than 10 years of age.

1. Introduction

Over the last century, intensive agricultural practices and increasing fossil fuel consumption have led to high levels of nonpoint source nutrient pollution, threatening drinking water quality, and contributing to the destruction of aquatic ecosystems from the local to the global scale [*Rockström et al*., 2009; *Howarth et al*., 2011; *Carpenter et al*., 2012; *Beusen et al*., 2016]. At the local level, high nutrient concentrations in agricultural runoff have increased the costs of drinking water treatment [*Heberling et al*., 2015] and, recently, have led to litigation calling for greater regulation of agricultural nutrient sources [*Stowe*, 2016]. At larger scales, nutrient loading to near-shore coastal waters has fed the growth of large hypoxic zones, decreasing marine biodiversity and altering ecosystem structures. Before 1970, there were only scattered reports of coastal hypoxia in the literature [*Rabotyagov et al*., 2010]; recent reviews, however, suggest that there may well be over 500 coastal "dead zones" worldwide, with the numbers doubling each decade [*Diaz and Rosenberg*, 2008; *Conley et al*., 2009]. While information gaps remain regarding the factors contributing to hypoxia, overwhelming evidence suggests that anthropogenic fertilization of marine systems by excess reactive nitrogen (N), defined as forms of N that are biologically, chemically, or radiatively active [*Galloway et al*., 2008], drives the onset and duration of hypoxic events in affected coastal waters [*Rabalais et al*., 2002; *Diaz and Rosenberg*, 2008].

In recent years, there has been increasing interest in linking riverine N export to current human-induced N inputs at the watershed scale [*Hong et al*., 2011; *Swaney et al*., 2012]. *Howarth et al*. [1996] and others have repeatedly demonstrated that net anthropogenic N inputs (NANI) to a watershed are good predictors of riverine N export across a range of watersheds [*Boyer et al*., 2002; *Billen et al*., 2009; *Hong et al*., 2013]. The majority of the NANI-based studies, however, have been carried out based only on snapshots in time or on multiyear averaging of N inputs and outputs, thus limiting their ability to effectively capture long-term responses to changes in inputs. Indeed, it is increasingly recognized that there may be decadal-scale time lags between changes in N inputs and measurable changes in water quality [*Meals et al*., 2010; *Fenton et al*., 2011; *Hamilton*, 2012; *Sanford and Pope*, 2013; *Van Meter and Basu*, 2015]. Such time lags have been attributed to the presence of both hydrologic and biogeochemical nutrient legacies within watersheds [*Basu et al*., 2010; *Worrall et al*., 2015; *Van Meter et al*., 2016; *Basu et al*., 2011; *Thompson et al*., 2011]. For

nitrogen, the hydrologic legacy corresponds to dissolved N, primarily in the form of nitrate, in the unsaturated zone and groundwater reservoirs, while the biogeochemical N legacy corresponds to the buildup of organic N in the root zones of soils, as has recently been shown in soils across the Mississippi River Basin [*Van Meter et al*., 2016]. Herein, legacy N is defined as N which remains within a watershed at least 1 year beyond its initial application at the land surface. It is important to realize, however, that legacy N in intensively managed landscapes may have a distribution of residence times, from 1 year to multiple decades or even multiple centuries, and can therefore serve as a long-term source to both surface and groundwater. Accordingly, a steady state approach to linking N inputs with outputs is inadequate for capturing time-lag effects on watershed-scale N dynamics and thus limits the predictive value of the established input-output relationship.

To overcome this limitation, some attempts have been made to interject a time component into the NANI-based approach. *McIsaac et al*. [2001], for example, developed a regression model for the Mississippi River Basin showing current-year N loading to be impacted by N surplus values for the previous 9 years. More recently, *Chen et al*. [2014] have employed cross-correlation analysis over a period of 30 years to determine the lag time between changes in N inputs and changes in riverine N export. Their analysis, in a study of the Yongan River watershed in eastern China, showed on average a 7 year lag between changes in net N inputs and changes in N export between 1980 and 2009. Although these results represent progress in linking long-term N input trajectories to N export, the modeling approach utilized by Chen et al. is regression based rather than process based and therefore does not explicitly account for or distinguish between biogeochemical and hydrologic time lags within the watershed and cannot explicitly predict how outputs will change in response to significant changes in inputs.

In general, models designed to assess changes in N concentrations and load in response to changes in N inputs as well as other management practices can be divided into three main categories: empirical models, conceptual models, and process-based models [*Cherry et al*., 2008; *Bouraoui and Grizzetti*, 2014]. Notable among the empirical models are the NANI-based models [*McIsaac et al*., 2001; *Boyer et al*., 2002; *Billen et al*., 2009; *Hong et al*., 2013; *Chen et al*., 2014], which develop nonphysically based transfer functions in order to predict outputs from known input data [*Bouraoui and Grizzetti*, 2014]. Conceptual models such as the Geospatial Regression for European Nutrient losses (GREEN) [*Bouraoui et al*., 2011] and MITERRA [*Velthof et al*., 2009] models are more complex than empirical models and may, for example, consider multiple pathways for nutrient transfer, use routing structures to establish spatial relationships between subbasins, or include simplified representations of key processes in different landscape compartments (land based versus aquatic) [*Bouraoui and Grizzetti*, 2014]. In contrast, process-based models such as SWAT [*Arnold et al*., 2012] explicitly simulate a large number of complex, physical processes, and attempt to represent a heterogeneous landscape, thus requiring a high level of parameterization.

The goal of the present study is to place current observed stream N dynamics in the context of long-term trajectories of N use. To achieve this goal, we have developed a parsimonious, process-based modeling approach that utilizes a limited number of parameters, thus allowing it run over long time scales with little input data. In addition, the model explicitly includes biogeochemical cycling within the soil profile as well as hydrologic transit times and watershed retention mechanisms in order to meaningfully account for legacies, time lags, and changes in N surplus values over time. By separating the soil and groundwater reservoirs, our modeling framework is in line with partitioned, conceptual models like the GREEN model, but with the addition of a more process-based approach. Such an approach is important in the context of watershed management, allowing us to more accurately quantify future changes in water quality based on current and future changes in input.

The first step in meeting the above goal was to quantify N inputs and outputs over a period of more than 200 years for two major U.S. watersheds, the Mississippi River Basin (MRB) and Susquehanna River Basin (SRB), which are the sources of significant nutrient contamination to the Gulf of Mexico and Chesapeake Bay, respectively. The second was to use these N input trajectories to drive a parsimonious, process-based model capable of accounting for N dynamics in subsurface reservoirs. In particular, our modeling approach allows us to chart decadal-scale changes in N magnitudes within the vadose zone and in groundwater, and to predict the timescales of change in surface water N loading in response to changes in land use and N management.

Through this work, we are attempting to answer the following questions: (1) How has N loading changed since preindustrial times, and what is the impact of N legacies on the loading trajectories for these two

watersheds? (2) What have been the magnitudes of N depletion and/or accumulation in soil and groundwater reservoirs across the study period (1800–2014)? (3) What are the estimated times of delivery of N within a watershed, from application at the land surface to exit at the catchment outlet, and how have these times changed over time? (4) How have the sources of N at the catchment outlet changed over time?

2. Model Development

The ELEMeNT modeling approach (Exploration of Long-tErM Nutrient Trajectories) utilizes a coupled framework (Figure 1) that pairs source zone dynamics, which include the accumulation and depletion of soil organic N (SON) within the root zone, with a travel time-based approach that accounts for transport and transformations along hydrologic pathways to determine N loading trajectories at the catchment outlet.

ELEMeNT is based on the fundamental principle that the behavior of the landscape at any point in time is a function not only of current conditions but also of past land use and nutrient dynamics contributing to the buildup or depletion of legacy stores in soils (biogeochemical legacy) and groundwater (hydrologic legacy). ELEMeNT's consideration of both current-year inputs as well as the role of legacy N stores in driving current nutrient fluxes distinguishes it from other watershed models and allows us to more effectively explore how fluxes may change over time as a function of land use and land management. To allow such consideration, each landscape unit in the ELEMeNT framework maintains a memory of past land use and management. Thus, although current land use for two landscape units may be the same, one may have undergone conversion from cropland back to nonagricultural land in 1950 and the other in 1980. Accordingly, these two areas would represent two different land use trajectories with different N legacies and thus different current N fluxes. To account for this diversity of past use, ELEMeNT treats the landscape not as a patchwork of spatial units based not on current land use (the most common approach) but as a distribution of unique land use trajectories, such that the model is able to maintain landscape memory and thus more adequately simulate legacy-related nutrient dynamics.

2.1. Outlet N Loading Trajectories: A Travel Time-Based Approach

To quantify nitrate-N load trajectories at the catchment outlet following land use change, ELEMeNT conceptualizes each point on the landscape as corresponding to an individual stream tube characterized by a unique travel time to the stream network [*Jury et al*., 1990; *Basu et al*., 2012; *Schilling et al*., 2012]. Within this framework, the landscape as a whole functions as a bundle of stream tubes having a unique distribution of travel times to the catchment outlet, $f(\tau)$. The travel time distribution, in turn, controls nitrate-N mass flux trajectories at the outlet, $M_{\text{out}}(t)$ [*Maloszewski and Zuber*, 1982; *Haitjema*, 1995; *McGuire and McDonnell*, 2006; *Van Meter and Basu*, 2015], as described by the following expression:

$$M_{out}(t) = \int_0^\infty J_s(t-\tau) f(\tau) e^{-\gamma\tau} d\tau + (1-k_h) W(t) \tag{1}$$

where $J_s(t-\tau)$ is the contaminant input function or "source function" that describes the mass flux of nitrate from the unsaturated zone to the groundwater, developed in section 2.2, γ [T^{-1}] is the first-order rate constant that describes N removal via denitrification along hydrologic pathways, $W(t)$ is human N consumption, and k_h is the denitrification rate constant for human waste (Figure 1). $W(t)$ is calculated based on annual population estimates, assuming human consumption rates of 5 kg ha^{-1} yr^{-1} [*Boyer et al*., 2002; *Hong et al*., 2011]. Wastewater N inputs are considered to directly enter surface waters, with negligible travel times to the catchment outlet.

It is important to note here that N retention in both surface water and groundwater is taken into account in the above equation through the use of γ and k_h as fitted, effective rate constants. More specifically, γ represents N removal in both groundwater and surface water, and k_h represents N removal from human waste via wastewater treatment plants as well as through in-stream N removal. Both of these parameters are fitted through model calibration based on measured N loading at the catchment outlet, as described below in section 3.3.2.

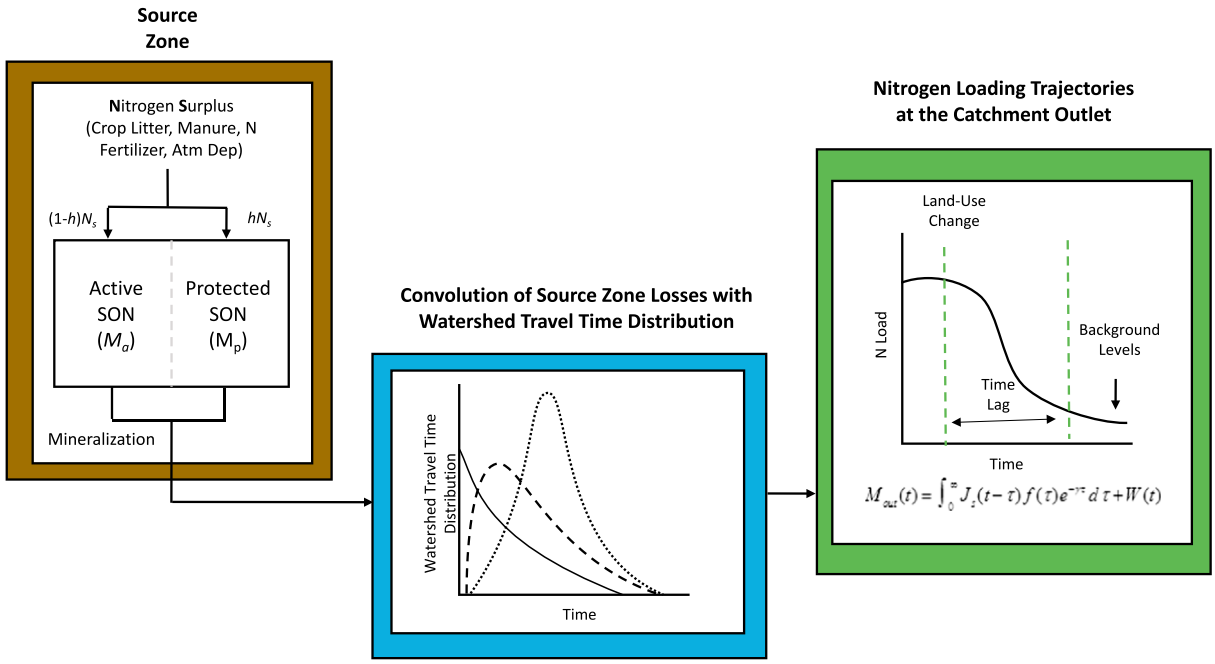

Figure 1. Conceptual framework for predicting catchment scale time lags as a function of hydrologic and biogeochemical legacies in the landscape. The source zone box (left) represents the flow of N through soil organic matter and the accompanying accumulation/depletion of biogeochemical legacy within the source zone. In this schematic, N_s represents the annual N surplus, and h is a "protection" coefficient, determining which portion of annual inputs enter the active, more metabolically active N pool, and which the more stable, protected pool of organic matter. Mass depletion from the source zone is convoluted with the groundwater travel time distribution (middle) to ultimately describe N loading trajectories at the catchment outlet (right).

2.2. Source Zone Dynamics

2.2.1. Watershed Land Use Trajectories

The watershed is segmented into s distinct units corresponding to distinct land use trajectories, and the temporal evolution of each unit is stored within a 2-D land use array, LU(s, t) representing a distribution of land use (cropland, pastureland, nonagricultural) over time (t) via the following equation:

$$\mathrm{LU}(s,t) = \begin{cases} 2 & s \leq A_{crop}(t) & \text{cropland} \\ 1 & A_{crop}(t) < s \leq \left[A_{crop}(t) + A_{past}(t)\right] & \text{pastureland} \\ 0 & s > \left[A_{crop}(t) + A_{past}(t)\right] & \text{other} \end{cases} \quad (2)$$

where A_{crop} and A_{past} correspond to watershed-scale percent cropland and percent pastureland, respectively. Land use data to create these trajectories is based on state-level cropland and pastureland data from U.S. Agricultural Census and Survey data (U.S. Department of Agriculture-National Agricultural Statistics Service (USDA-NASS)), supplemented by historical modeled cropland data from *Ramankutty and Foley* [1999], aggregated to the watershed scale.

2.2.2. Estimation of the Source Function

Each of the s distinct LU trajectories have a corresponding J_s (s, t) that describe the mass leaching from the unsaturated zone at any time t, such that the source function, which is the watershed-scale mass leaching from the source zone to the groundwater J_{s_wshd} (kg/ha), can be estimated as the sum of the source zone values across the distribution of land use trajectories (s):

$$J_{s_{wshd}}(t) = \sum_{s=1}^{1000} J_s(s,t) \quad (3)$$

ELEMeNT utilizes a parsimonious modeling framework (Figure 2) to estimate the biogeochemical legacy mass residing in the source zone and the mass leaching from the source zone at any time t, $J_s(s,t)$. The mass residing in the source zone is the sum of the mass in the soil organic matter, $M_{\mathrm{SON}}(s,t)$ and the mass in the mineral pool, M_s (s,t). The soil organic matter pool can further be conceptualized as the sum of an active pool $M_a(s, t)$ (kg ha^{-1}) with faster reaction kinetics and a more protected passive pool $M_p(s, t)$ (kg ha^{-1}) with slower kinetics. In the following sections, we develop the equations for $\mathrm{M_a}$, M_p, M_s, and J_s.

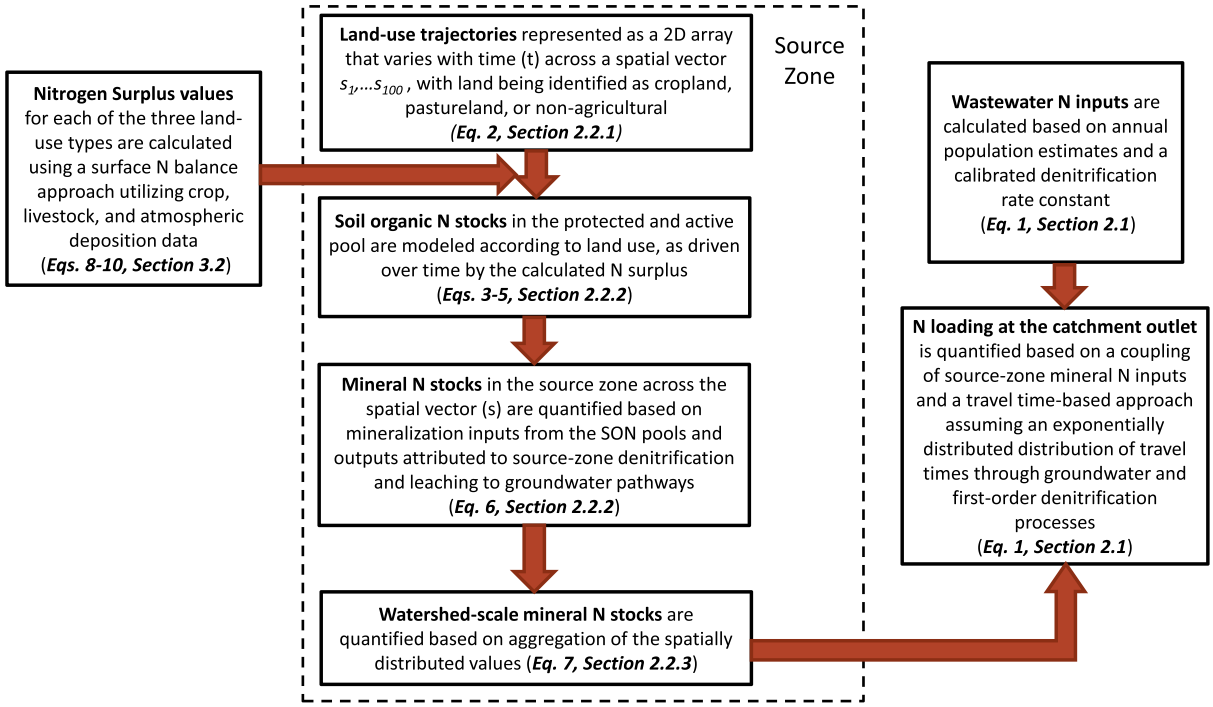

Figure 2. The ELEMeNT modeling framework.

Within this framework, we consider that all of the annual N surplus (N_s (i, t), kg ha^{-1} yr^{-1}; I = 0, 1, 2 for the three LU types considered) cycles through either the active or protected SON pools, with the outputs being inorganic N $M_s(s, t)$ produced by the mineralization of SON. This pathway is consistent with the results of isotope studies indicating that the majority of NO_3^- leachate has undergone biogeochemical transformation within the soil organic pool before being mineralized and lost from the system [*Haag and Kaupenjohann*, 2001; *Spoelstra et al.*, 2001]. Mineralization is conceptualized as a first-order process with the rate constants k_a (year^{-1}) and k_p (year^{-1}). Partitioning of the annual N surplus between the active and protected pools is considered to occur as a function of land use and tillage practices [*Janssen*, 1984; *Six et al.*, 2002] and is represented within the model via a protection coefficient, h, the value of which is determined based on model calibration, as described in section 3.3.

Using this framework, N dynamics for the active and protected pools of SON across the distribution of land use trajectories, s, can be represented via the following differential equations:

$$\frac{dM_p(s,t)}{dt} = \begin{cases} hN_s(\mathrm{LU}(s,t),t) - k_p M_p(s,t), & \mathrm{LU}(s,\ t-1) = 2 \\ hN_s(\mathrm{LU}(s,t),t) - \left(M_p(s,t) - 0.7M_{p\_\mathrm{prist}}\right), & \mathrm{LU}(s,t) = 2 \ \text{ and } \ \mathrm{LU}(s,t-1) = 0,1 \end{cases} \tag{4}$$

$$\frac{dM_a(s,t)}{dt} = \begin{cases} (1-h)\,\mathrm{NS}(s,t) - k_a M_a(s,t), & \mathrm{LU}(s,t)\leq 1,\ \ \mathrm{LU}(s,t) = 2 \ \text{ and } \ LU(s,\ t-1) = 2 \\ (1-h)\,\mathrm{NS}(s,t) + \left(M_p(s,t) - 0.7M_{p\_\mathrm{prist}}\right), & \mathrm{LU}(s,t) = 2 \ \textit{ and } \ LU(s,t-1)\leq 1 \end{cases} \tag{5}$$

where M_{p_prist} (kg/ha) corresponds to the protected soil N stocks under pristine land use conditions and h is the protection coefficient. The annual N surplus array, N_s(LU(s, t),t), is developed based on land use-specific N surplus values, calculated as described in section 3.2.

Within this conceptual framework, which focuses on changing dynamics between cultivated and noncultivated landscapes, ELEMeNT considers physical protection mechanisms such as soil aggregation to be the primary determinant of whether SON remains within the protected pool [*Six et al.*, 2002]. When land is transitioned from pastureland (LU = 1) or nonagricultural land use (LU = 0) to cropland (LU = 2), we assume physical protection mechanisms to be disrupted, leading M_p to be reduced, in a step function, to 70% of the protected SON stock under the pristine condition (M_{p_prist}). Such an assumption is based on empirical

evidence across multiple landscapes of fast decreases in SON on this order of magnitude after initial cultivation [*Whitmore et al*., 1992; *Davidson and Ackerman*, 1993; *Beniston et al*., 2014]. Within the modeling framework, this mass of N from the protected pool is transferred to the active pool upon cultivation, making it subject to fast mineralization. Accordingly, just as the net N inputs are partitioned between the active and protected pools as a function of land use, the partitioning of SON stocks between the pools also changes as a function of changes in land use. These dynamics are expressed in equations (4) and (5) above.

Nitrogen leaving the SON pool enters the source zone mineral N pool (M_s), from which it will either leach into groundwater or leave the soil system via denitrification. Source zone N trajectories can be described using the following equation:

$$\frac{dMs(s,t)}{dt} = k_a M_a(s,t) + k_p M_p(s,t) - \lambda_s M_s(s,t) - J_s(s,t)$$
$$J_s(s,t) = \begin{cases} M_s(s,t)\dfrac{Q(t)}{V_w}, & Q(t) < V_w \\ M_s(s,t), & Q(t) > V_w \end{cases} \quad (6)$$

where $\lambda(t)$ (year^{-1}) is the denitrification rate constant in the source zone, $Q(t)$ is the annual discharge and V_w ($= nsV$) is the water volume in the source zone, with n being the porosity, s the saturation, and V the volume of the soil column per unit area within the source zone. Here the first two terms on the right-hand side of the top equation represent the input from the active and protected organic pools, protected pools, the third term is the loss from the source zone via denitrification, and the last term is losses from leaching to groundwater. Note that when annual flow is greater than the water volume in the source zone, the mass of mineral N in the source zone goes to zero.

3. Methods and Data Sources

3.1. N Mass Balance

Annual N surplus values (NS) were calculated using a surface N balance approach [*Bouwman et al*., 2005], which considers N inputs and outputs to the landscape, with the N surplus being defined as N inputs − usable outputs [*Parris*, 1998; *Erisman et al*., 2005; *Leip et al*., 2011]. Using this approach, inputs are calculated separately for cropland, pastureland, and nonagricultural land:

$$N_s(\text{crop}, t) = \text{BNF}_{crop} + \text{FERT}_{crop} + \text{MAN}_{crop} + \text{DEP} - \text{CROP} \quad (7)$$
$$N_s(\text{past}, t) = \text{BNF}_{past} + \text{FERT}_{past} + \text{MAN}_{past} + \text{DEP} - \text{GRASS} \quad (8)$$
$$N_s(\text{other}, t) = \text{BNF}_{nat} + \text{DEP} \quad (9)$$

where N_s(crop, t), N_s($past$, t), and N_s(other, t) represent surplus N applied to cropland, pastureland, and nonagricultural land, respectively, at the soil surface; BNF_{crop}, BNF_{past}, and BNF_{nat} refer to biological nitrogen fixation; $\text{FERT}_{\text{crop}}$ and $\text{FERT}_{\text{past}}$ refer to applied inorganic N fertilizer; MAN_{crop} refers to manure applied to cropland; MAN_{past} refers to manure applied to cropland as well as animal N excreted during grazing; DEP refers to atmospheric N deposition; CROP refers to crop N output; and GRASS (kg/ha) to grass N consumption by grazing livestock, all in units of kg ha^{-1}.

Biological N fixation (BNF), the process by which nonreactive atmospheric N is converted to reactive N via microbial activity [*Galloway et al*., 1995], was calculated based on state-level cropped area and crop production data obtained through the U.S. Agricultural Census (http://www.nass.usda.gov) and U.S. Agricultural Survey [*U.S. Department of Agriculture-National Agricultural Statistics Service (USDA-NASS)*, 2016] using area and yield-based methods [*Bouwman et al*., 2005; *Han and Allan*, 2008; *Hong et al*., 2013]. Fertilizer N inputs (FERT) are based on county-level estimates of N fertilizer application for the conterminous U.S. [*Ruddy et al*., 2006] as well as Food and Agriculture Organization estimates of mean N fertilizer application to pastureland [*Francis*, 2000; *Food and Agriculture Organization*, 2006]. Manure N inputs (MAN) were calculated based on livestock data from the U.S. Agricultural Census (http://www.nass.usda.gov) and U.S. Agricultural Survey [*USDA-NASS*, 2016], animal N intake and excrement parameters [*Smil*, 1999; *Bouwman et al*., 2005; *Hong et al*., 2011], and estimates regarding the distribution of livestock between unconfined and confined feeding operations [*Kellogg et al*., 2000]. Removal of N via crop production (CROP) and grazing (GRASS) was calculated using census data for harvest yields and livestock production (USDA-NASS) and relevant parameter values for

crop N content and livestock grass consumption obtained from the literature [*Bouwman et al*., 2005; *Hong et al*., 2011]. For further details regarding calculations for the N mass balance, see Text S1 in the supporting information.

3.2. Uncertainty Analysis for the N Mass Balance

Uncertainty analysis, utilizing Monte Carlo simulations, was carried out to characterize the uncertainty associated with the calculation of N surplus values [*Mishra*, 2009; *Chen et al*., 2014]. For each parameter used in the mass balance calculations, we assumed a normal probability distribution with a coefficient of variation (CV) value of 0.3. A total of 1000 simulations were carried out to obtain median and interquartile range values for the N surplus trajectory across the study period.

3.3. Sensitivity Analysis and Model Calibration

3.3.1. Sensitivity Analysis

Global parameter sensitivity analysis was carried out to identify model parameters contributing most significantly to soil organic N (SON) levels and stream N loading [*Muleta and Nicklow*, 2005; *Mishra*, 2009]. As given in Tables S2.1 and S2.2 in the supporting information, 10 potentially calibratable parameters were chosen from the model and were assumed to follow a uniform distribution across a designated range [*Haan et al*., 1998]. Ranges for each parameter were assigned based on a combination of literature review and knowledge of the two study watersheds. The Latin hypercube sampling technique, a form of stratified Monte Carlo sampling, was used to generate 1000 parameter sets from these ranges, assuming a uniform distribution across each range. The model simulations were then run, and the output variables of interest (residual sum of squares values for (1) median SON values, 1950–2015; (2) SON accumulation, 1980–2010; and (2) annual N loading at the catchment outlet) were extracted. Output data were rank transformed to account for nonlinearities in model behavior [*Iman and Conover*, 1979; *Muleta and Nicklow*, 2005]. Stepwise regression analysis was carried out with the 1000 input-output pairs for both SON values and annual N loading. A threshold value of $p \leq 0.05$ was used as criteria for inclusion of individual parameters in the model. Results of the regression analysis are given in Tables S2.3 and S2.4 in the supporting information.

3.3.2. Model Calibration

Model parameters were selected for optimization based on the results of the sensitivity analysis. The model was calibrated to optimize simulation of (1) current levels of SON and (2) N loading at the catchment outlet. Median SON levels for the watersheds were calculated based on USDA gridded soil survey data [*Soil Survey Staff*, 2015]. For the MRB, catchment N loading values are based on U.S. Geological Survey (USGS) water quality data (Mississippi River near St. Francisville, Louisiana, and Atchafalaya River at Melville, Louisiana) and discharge data (Mississippi River at Tarbert Landing, Old River Outflow Channel near Knox Landing, Atchafalaya River at Simmesport, Ohio River at Metropolis, and Mississippi River at Thebes) via the regression-based rating-curve method [*Aulenbach*, 2006; *United States Environmental Protection Agency (USEPA)*, 2014]. For the SRB, N loading was calculated at Conowingo by the weighted regressions on time, discharge and season (WRTDS) method [*Hirsch et al*., 2010] via the EGRET software package [*Hirsch and De Cicco*, 2014]. The mean absolute error was used as the objective function to assess goodness of fit to the observed data from a series of Monte Carlo simulations. Optimization was carried out in an iterative fashion, with the top-performing 10% of parameter sets from each set of simulations being selected based on goodness of fit to the specified objective function. Median values were extracted for all relevant parameters, as provided in Table S2.5 in the supporting information.

3.4. Site Descriptions

3.4.1. Mississippi River Basin

The Mississippi River Basin (MRB), which covers approximately 40% of the land area of the contiguous U.S. (2,981,076 km^2) is an intensively managed system that over the last 200 years has undergone radical transformation, both terrestrially and hydrologically. In 1866, cropped area in the MRB made up only 6% of watershed area (Figure 4). By 1940, however, the area in cropland had nearly quadrupled. Between 1866 and 1890, the rate of increase was at its greatest, resulting in close to 15,000 km^2 of land—the equivalent of the state of Connecticut—being brought under new cultivation each year. The MRB now accounts for approximately 70% of U.S. cropland and contains approximately 60% of all cattle of 90% of all hogs raised within the U.S. [*Smith et al*., 2005]. Soil in the MRB is highly fertile, with soil organic carbon (SOC) content ranging from median values of 7.1 kg m^{-2} (~0.7 kg m^{-2} SON) in the Tennessee River subbasin to 12.5 kg m^{-2} (~1.0 kg m^{-2} SON) in

the Missouri River subbasin [*Buell and Markewich*, 2003]. Widespread agricultural land use in the basin has led to high levels of fertilizer application and intensive livestock production, resulting in high levels of nutrient loading to offshore waters [*Rabalais et al*., 2002]. Currently, the Mississippi delivers more than 900 megaton of N to the Gulf of Mexico each year, with a long-term mean discharge volume of 17,000 m^3/s (~180 mm yr^{-1}) [*Goolsby et al*., 1999; *Turner and Rabalais*, 2003; *Murphy et al*., 2013].

3.4.2. Susquehanna River Basin

The Susquehanna River Basin (SRB) (70,160 km^2), extends through portions of Maryland, Pennsylvania, and New York and empties into the northern region of the Chesapeake Bay, immediately downstream from the Conowingo dam [*Foster et al*., 2000]. With a daily mean discharge of 1030 m^3/s (~460 mm yr^{-1}), the Susquehanna is the largest river draining into the Chesapeake Bay and accounts for more than half of the annual nutrient load to the bay [*Foster et al*., 2000; *Kemp et al*., 2005; *Zhang et al*., 2016]. Soil fertility in the SRB is significantly lower than that in the MRB, with median SOC and SON levels of approximately 2.6 kg m^{-2} and 0.2 kg m^{-2}, respectively, less than one fourth levels in the MRB. Agricultural land use in the SRB peaked early in the twentieth century [*Houghton and Hackler*, 2000; *USDA-NASS*, 2016] (Figure 3). Since then, the basin has experienced both increasing urbanization and widespread reforestation of previously cleared land [*D'elia et al*., 2003; *Kemp et al*., 2005; *Drummond and Loveland*, 2010; *Thompson et al*., 2013]. Despite the declining proportion of the watershed devoted to agriculture (from 24% in 1918 to approximately 11% in 2014) [*Ramankutty and Foley*, 1999], increased use of commercial fertilizers and importation of animal feed paired with high levels of atmospheric N deposition have led to anthropogenically induced increases in primary productivity and associated problems of hypoxia in the Chesapeake Bay [*Kemp et al*., 2005; *Zhang et al*., 2016]. For details regarding these changes in inputs, see section 4.1 and Figure 4.

4. Results and Discussion

The objective of the present study was to develop a modeling framework, ELEMeNT, to quantify long-term, watershed-scale N fluxes and to use this new framework to quantify N legacies and to assess their impacts on water quality. To carry out this objective, we synthesized land use, population, and agricultural production data to create soil surface N surplus trajectories for the years 1800–2015 across the Mississippi and Susquehanna River Basins. These input trajectories were then used to model N dynamics across the study period. As described below, the model results allow us to quantify depletion and accumulation trajectories of subsurface N stores. In addition, model results allow us to explore questions regarding the travel times of N from its entry into the terrestrial system to its exit at the catchment outlet, as well as the sources of annual N outputs.

4.1. Cropland N Surplus Trajectories

Cropland N surplus trajectories in both MRB and SRB are characterized by large increases in N inputs between 1945 and 1980, primarily driven by increases in fertilizer application during this period (Figure 4). Interestingly, it can be seen that despite differences in climate, land use, and soil fertility between the two watersheds, N surplus values for cropland are quite similar. For example, for the period 1990–2014, the mean N surplus for cropland was 63.7 ± 15.4 kg ha^{-1} yr^{-1} for the MRB and 78.2 ± 18.5 kg ha^{-1} yr^{-1} for the SRB. The relative importance of specific sources of N, however, does vary between watersheds. For example, the mean rates of fertilizer application to cropland in the MRB during this period were approximately 25 kg ha^{-1} higher in the MRB than in the SRB (Figure 5). Other N inputs (BNF, Manure N, and atmospheric N deposition), however, were all greater in the SRB, making up this difference and ultimately leading to a somewhat higher N surplus for SRB cropland. Both manure (14.6 ± 0.6 kg ha^{-1} yr^{-1}, SRB; 5.1 ± 0.2 kg ha^{-1} yr^{-1}, MRB) and biological N fixation (88.9 ± 1.9 kg ha^{-1} yr^{-1}, SRB; 79.2 ± 7.0 kg ha^{-1} yr^{-1}, MRB) from the growth of N-fixing crops such as alfalfa and soybean account for a larger proportion of N inputs to cropland in the SRB than the MRB due to higher densities of livestock production in the SRB and the smaller area of land in agricultural production available for manure application.

Atmospheric N deposition was found to be a particularly important portion of the N budget in the SRB, accounting for approximately 13% of N inputs to cropland from 1990-2014 (23.0 ± 5.6 kg ha^{-1} yr^{-1}) compared to the 6% of inputs (10.6 ± 1.1 kg ha^{-1} yr^{-1}) in the MRB, primarily due to high nitrogen oxide emissions from fossil fuel combustion in the northeastern United States [*Jaworski et al*. 1997]. Interestingly, atmospheric N deposition has decreased in both watersheds over the last several decades, with decreases of 15% in the

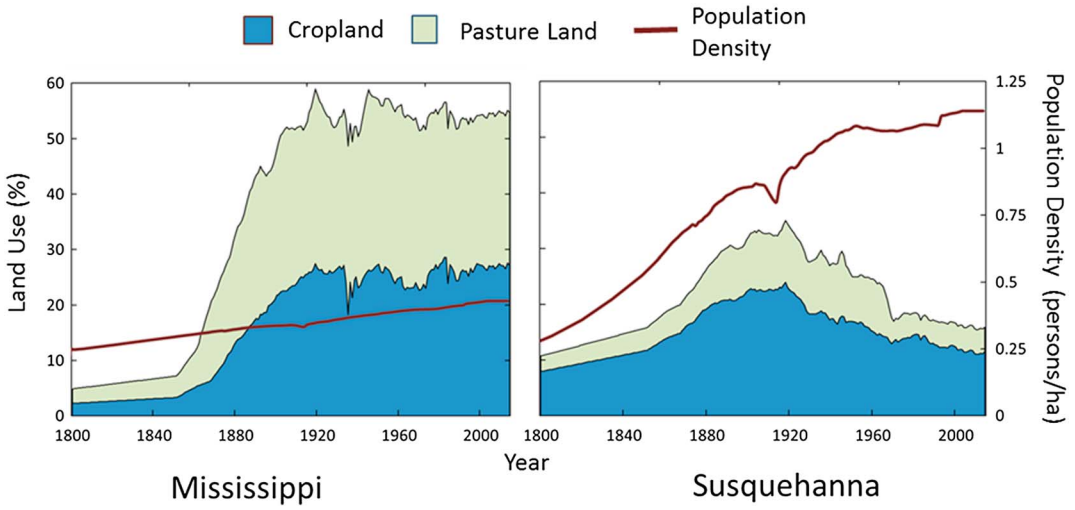

Figure 3. Land use and population trajectories for the Mississippi and Susquehanna River Basins. Cropland and pastureland land use trajectories are based on state-level cropland and pastureland data (USDA-NASS), supplemented by historical modeled cropland data from *Ramankutty and Foley* [1999], aggregated to the watershed scale.

MRB and a noteworthy 45% in the SRB since 1990. Our findings show that NH_x deposition, which is strongly linked to agricultural practices, actually remained constant at approximately 5 kg ha^{-1} over this period in the SRB. In contrast, NO_x deposition, which is primarily linked to fossil fuel combustion, decreased from 28 kg ha^{-1} in 1990 to 13 kg ha^{-1} in 2014. Such decreases are being attributed to both the successful implementation of air pollution emission controls in contributing areas as well as to recent climate-related shifts in atmospheric circulation patterns over areas of North America [*Lloret and Valiela*, 2016].

4.2. Sensitivity Analysis and Model Calibration

Sensitivity analysis showed that the primary parameters impacting 1950–2010 median SON levels were the mineralization rate constants (k_a, k_p) for active and protected SON and the humification coefficients for noncultivated and cultivated land (h_{nc}, h_c) (Tables S2.3 and S2.4 in the supporting information). N loading at the catchment outlet was found to be chiefly impacted by denitrification rate constants in soil and groundwater (λ_s,) as well as the mean travel time (μ) through hydrologic pathways, which can include the shallow subsurface, deeper groundwater, and surface water.

Calibration results for the model are given in Table S2.5 in the supporting information. Calibrated parameter values are of the same order of magnitude between the two basins. The most significant difference in parameterization for the two basins is in the soil mineralization rate constant, k_p, for protected soil, which is more than 6 times greater for the SRB than for the MRB (1.4×10^{-4} yr^{-1}, MRB; 9.2×10^{-4} yr^{-1}, SRB). This difference accounts for the much higher levels of levels of soil organic matter and thus higher fertility in soils of the MRB.

Modeled and measured N loads at the outlets of the Mississippi and Susquehanna River Basins are shown as a function of time in Figure 5. Plots of modeled versus measured loads are also provided in Figure S3.1 in the supporting information. In Figure 5, modeled loads are shown for the entire study period (1800–2014), and annual estimates based on measured concentration values are provided where available. For the MRB (Figure 5a), measured data for the period 1979–2013 indicate median nitrate-N loading to the Gulf of Mexico of 3.3 kg ha^{-1} yr^{-1} (980 kt yr^{-1}). These results are well matched by the model results, which predict loading of 3.2 kg ha^{-1} yr^{-1} (968 kt yr^{-1}), a difference of only 1.3%. For the SRB, measured data indicate N loading of 6.0 kg ha^{-1} yr^{-1} (42.9 kt yr^{-1} for the period 1979–2013 (Figure 5b), compared with the model-predicted loading of 6.2 kg ha^{-1} yr^{-1} (43.0 kt yr^{-1}), a difference of only 2.5%.

It should be noted here that model calibration was carried out for both basins for the years 1979–2013. Although for the SRB no measured data are available before that period, we do have estimates of annual N loading for the MRB back to 1955, which allows us the opportunity to validate the model during a period with a significantly different N input regime. More specifically, the annual catchment-scale N surplus in the

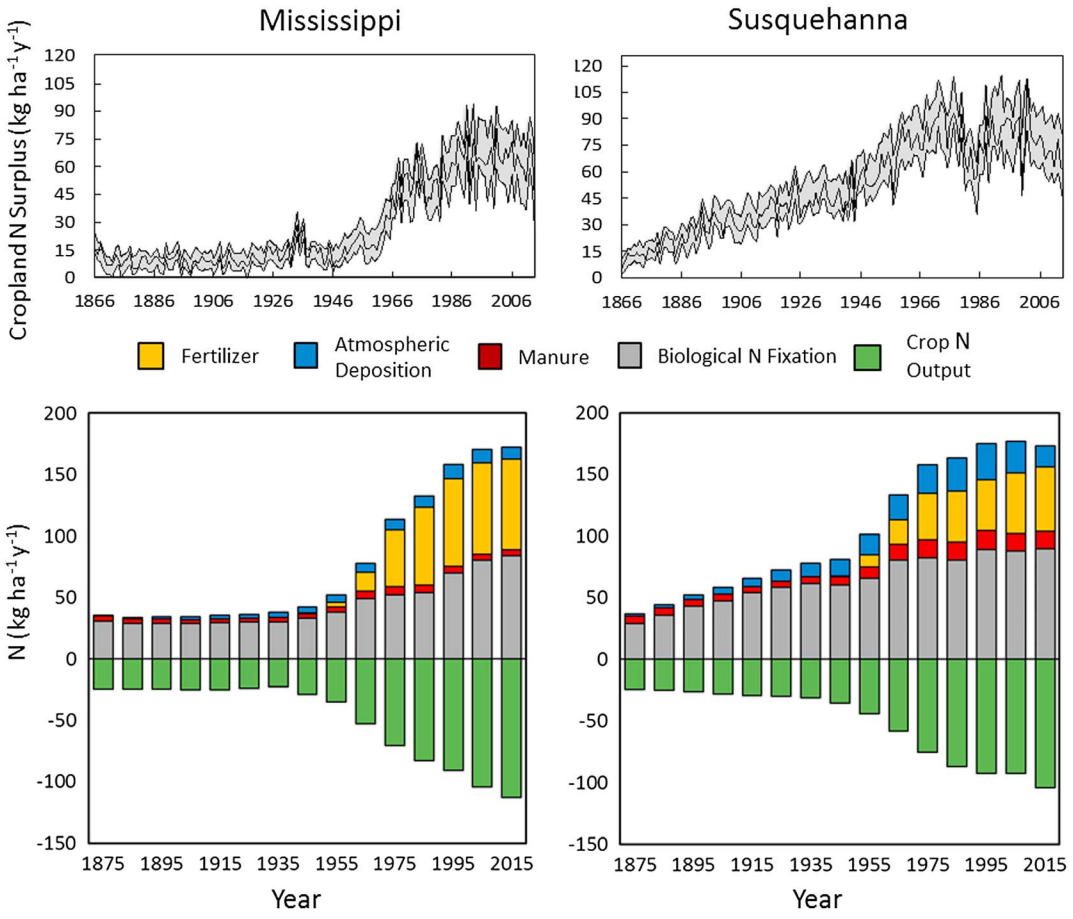

Figure 4. Nitrogen inputs to agricultural land, 1866–2014. The figure shows net N input trajectories for both Mississippi and Susquehanna River Basins (top). In the bottom, individual components for the N balance are shown, with inputs (fertilizer, atmospheric deposition, manure, and biological N fixation) represented by the stacked lines and crop N outputs represented by white bars.

MRB was only 16.5 ± 2.3 kg ha^{-1} for the period 1955–1970, approximately half that calculated for the later calibration period (29.6 ± 3.3 kg ha^{-1}). Modeled values for 1955–1970, however, show an excellent match with measured values (1.2 ± 0.2 kg ha^{-1}, modeled; 1.1 ± 0.3 kg ha^{-1}, measured), a statistically insignificant difference, despite the much lower N fertilization rates for the 1955–1970 period and the rapid changes in management practices during this period, including a major shift from the growth of small grains such as barley and wheat to the more widespread cultivation of N-fixing soybeans [*Foufoula-Georgiou et al.*, 2015]. The good model fit for this period suggests that our pre-1955 trajectories are also defensible and provide a good estimate of long-term N loading trajectories for the MRB.

4.3. Nitrogen Fluxes and Stores

4.3.1. Stream N Loading

The long history of N input data developed herein for the Susquehanna and Mississippi River Basins together with the ELEMeNT modeling framework allows us to provide a historical reconstruction of nitrate-N loading over the past two centuries. Using this approach, we are able not only to estimate preindustrial N loading levels but also to better understand trajectories of change for the rivers themselves and for receiving water bodies.

In the present study, our model results suggest that preindustrial (1800–1840) riverine nitrate fluxes were on the order of 0.5 kg ha^{-1} yr^{-1} for both of the study basins, corresponding to concentrations of approximately ~0.4 mg L^{-1} and MRB and ~0.1 mg L^{-1} in the SRB). These results indicate that nitrate-N loads have increased approximately sevenfold in the MRB since 1840 and more than fourteenfold in the SRB since the preindustrial

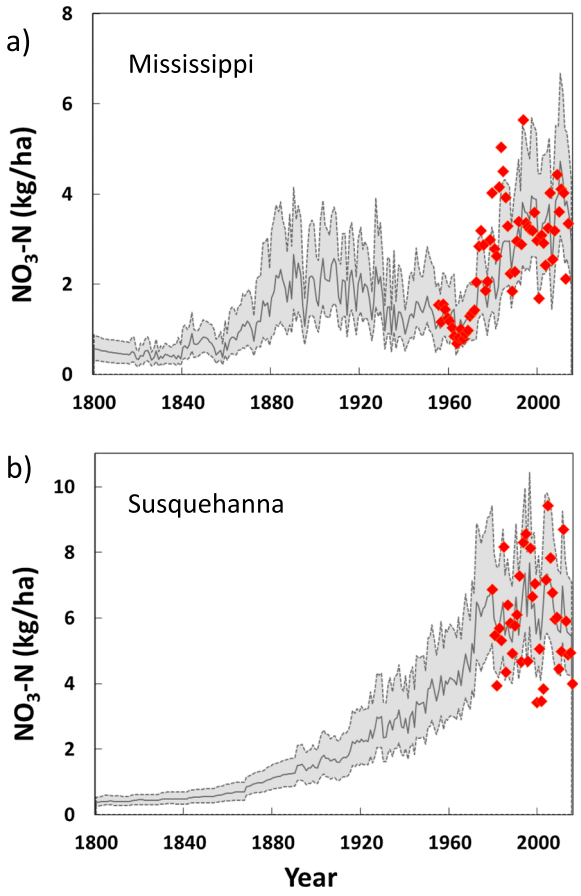

Figure 5. Catchment-scale N loading to the Mississippi and Susquehanna River Basins, 1800–2014. Load values are area-normalized to the total catchment area for (a) Mississippi and (b) Susquehanna. Red diamonds represent measured N loads for the two basins, while the black line represents the modeled values. The grey area indicates the 95% confidence interval based on the calibrated parameter values.

period. Our modeled estimates are in line with previous estimates by *Howarth et al*. [1996], who have reported twofold to twentyfold increases in N fluxes in North Atlantic watersheds, and those by *Kemp and Dodds* [2001], whose data show sixfold to fortyfold increases in nitrate-N in North American prairie streams. Both of these earlier estimates are based on space-for-time substitutions, which assume that current N fluxes from pristine or near-pristine catchments can accurately represent historical conditions.

While such large increases in N loading between the current and the preindustrial periods are expected, the trajectories of change for the two basins may be considered surprising. First, although the fastest twentieth century rates of change in loading for both watersheds occurred between approximately 1960 and 1980 (~3–5% increases in nitrate-N loading each year), corresponding to large increases in commercial fertilizer application during this period (Figure 2), our results suggest that N loading prior to this period was already elevated approximately 3 to 4 times above baseline levels ($1.4 \pm 140\,\mathrm{kg\,ha^{-1}\,yr^{-1}}$, MRB; $2.8 \pm 0.3\,\mathrm{kg\,ha^{-1}\,yr^{-1}}$, SRB). For the SRB, increases in N loading were relatively linear from 1850 to 1950, reflecting a steady intensification of agriculture as well as N deposition from industrial sources. For the MRB, however, the loading trajectory appears to have been more threshold based, coinciding with the plowing of North American prairie lands, and a sharper land use change trajectory. As seen in Figure 6, nitrate-N loads more than tripled between 1850 and 1890 and then decreased again to near-pristine levels until the widespread adoption of commercial N fertilizer use in the mid-twentieth century.

This early increase in N loading for the MRB corresponds to a period of fast and far-reaching land use change, as pristine or minimally impacted lands were converted to row crop agriculture across the basin, and is comparable to the increases observed following the widespread plowing of permanent grasslands in the UK after

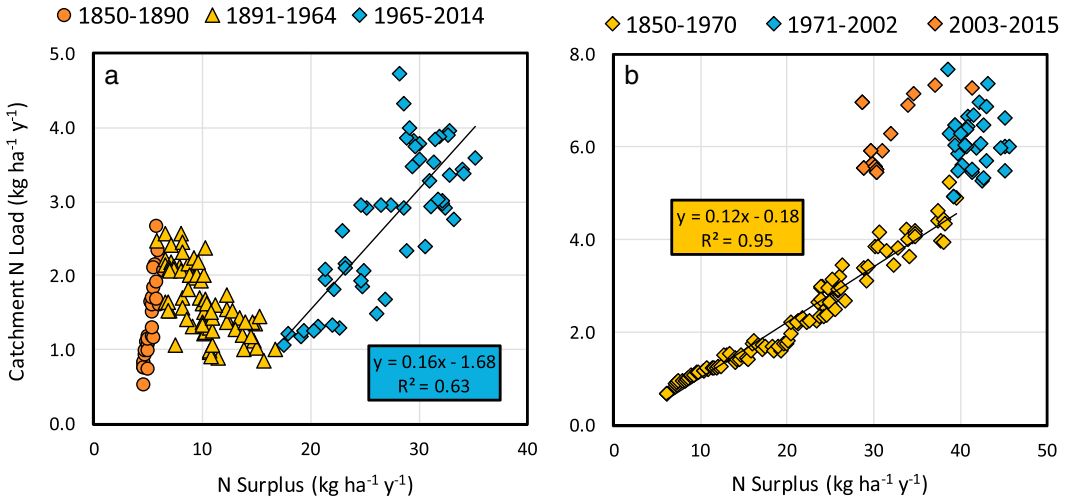

Figure 6. Relationship between N loading at catchment outlet and N surplus values. For (a) the MRB, N loading shows a strong linear relationship ($p < 0.001$, and $R^2 = 0.63$) between 1965 and 2014. Similarly, a direct linear relationship can be seen for (b) the SRB from 1860 to 1970 ($p < 0.001$, and $R^2 = 0.96$). Outside of these periods, however, N loading is decoupled from annual N surplus values due to the impacts of large landscape-scale release of SON (MRB) and, more recently in the SRB, anthropogenic N legacies. In particular, a pattern of hysteresis can be seen for the SRB since 1971 (blue diamonds), as N loading remains elevated despite decreases in the N surplus.

World War II [*Howden et al*., 2011]. Such large, landscape-scale losses of N are also similar to those currently being seen in the Amazon basin, which has begun to show elevated N loading due to the effects of deforestation and new cultivation, despite the overall N surplus for the region remaining relatively low [*Howarth et al*., 1996; *Biggs et al*., 2004; *Fonseca et al*., 2014]. Our finding of a mid-nineteenth century increase in N loading for the MRB is also supported by increases in the levels of biologically bound silica that have been found in marine sediments in the Gulf of Mexico from this period [*Turner and Rabalais*, 2003]. As N is the nutrient that most frequently limits primary productivity in near-coastal waters [*Mitsch et al*., 2001; *Howarth et al*., 2006], Bsi levels, which are directly linked to levels phytoplankton production, can be used as a proxy measure of N loading to these waters.

A decoupling of N surplus values from nitrate-N loads due to N legacy or N storage-related effects can be seen for both the MRB and SRB in Figure 6. In the figure, nitrate-N loading at the catchment outlet is plotted against the annual N surplus, with the slopes of the regression lines corresponding to the percent of the N surplus being lost as riverine output. For the period 1965–2014, the MRB N load shows a strong relationship with N surplus values (slope = 0.16, $R^2 = 0.63$, and $p < 0.001$) (Figure 6a). Prior to this period, however, N loading is largely decoupled from N inputs. From 1850 to 1890, for example, the fast rate at which land was brought under cultivation and the high levels of SON in prairie soils led to an additional 9000 kt of N reaching the mouth of the Mississippi compared with N loading for the previous 40 years, despite only minimal increases in the overall N surplus. Accordingly, the regression line for the load versus surplus relationship is nearly vertical for this period (slope = 0.92), reflecting the large-scale release of landscape N legacies. In the subsequent period, during which this newly released N began leaving the system, N loading actually shows an inverse relationship with surplus values, with legacy N dynamics completely masking the more direct input-out relationship.

For the SRB, new cultivation during the preindustrial period occurred over longer time scales and soil N stores in pristine land were less than a third those in the MRB, leading to a much lower impact of cultivation on early N dynamics. Accordingly, N loading is strongly correlated with annual N surplus values before approximately 1970 (slope = 0.12, $R^2 = 0.96$, and $p < 0.001$) (Figure 6b). After 1970, however, N surplus values began to level off (1971–1989) and then to decrease (1990–2014), primarily due to decreases in atmospheric N deposition rates. During these periods, catchment-scale N loading began to be more strongly driven by N legacies than by current year N inputs. In the figure, this shift is reflected by the nonlinear relationship between surplus values and N loading after 1970. The pattern of response between surplus values and N loading plotted in

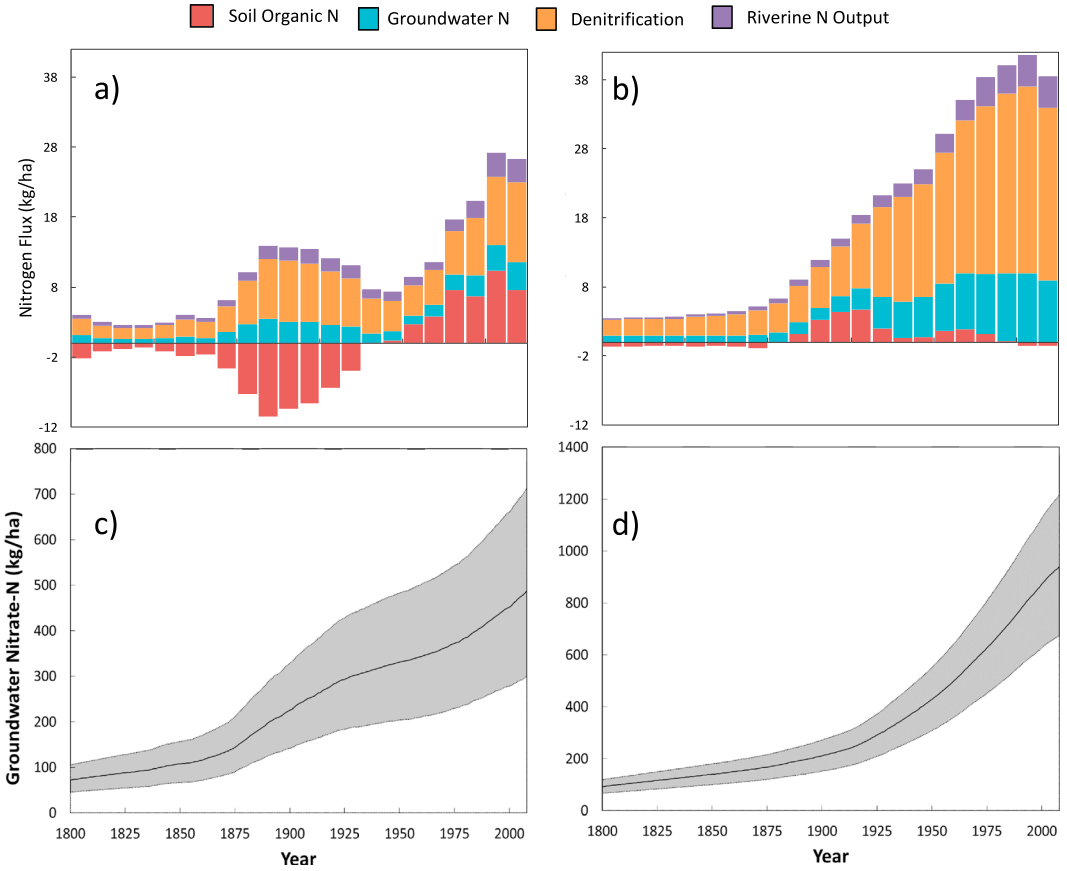

Figure 7. Nitrogen fluxes to and from subsurface reservoirs in the Mississippi and Susquehanna River Basins, 1800–2014. (a) For the MRB, soil organic N fluxes exhibit a major regime shift over the study period, from a depletion pattern from the 1880s to 1930s, to a pattern of N accumulation since the 1960s. (b) For the SRB, soil N plays a more minor role in N dynamics, with groundwater functioning as a more significant N sink. Our modeling results show groundwater N accumulation in (d) the SRB to be approximately twice that in (c) the MRB.

the figure is hysteretic, with the counter-clockwise path of the response loop suggesting a time delay in the recovery trajectory for the basin, despite clear reductions in N surplus values. Such nonlinearities between N inputs and outputs has also been observed by *Zhang et al.* [2016] at multiple sites within the SRB.

4.3.2. Regime Shifts in Soil Organic N Trajectories

For the MRB, the model results show a pattern of soil organic N (SON) depletion after initial cultivation of pristine landscapes (Figure 7a), followed by SON accumulation as net N inputs increase. This pattern is suggestive of three different functional states across the anthropogenically induced evolution of the landscape [*Van Meter et al.*, 2016]. In the first, under pristine or very low impact conditions, SON levels were at steady state, with rates of immobilization and mineralization being equal to each other such that there is minimal net N flux out of the soil organic pool. In the second, which for the MRB began in the middle to late 1800s and which was triggered by the rapid westward expansion of settlement across the watershed, was characterized by a large regime shift, where the soil layer became a major source of mineralized N to surface and groundwater. These results are in line with many literature reports of rapid mineralization of soil organic matter after initial cultivation [*Whitmore et al.*, 1992; *Davidson and Ackerman*, 1993; *Lal et al.*, 2003; *David et al.*, 2009; *Beniston et al.*, 2014], particularly in nutrient-rich soils like those found throughout the North American prairie region. Such rapid losses can be attributed to a loss of the physical protection provided by soil aggregates in undisturbed soils, as cultivation breaks up aggregate structures [*Six et al.*, 2002] and thus increases oxidation and mineralization rates [*Lal et al.*, 2003]. Finally, in the third stage, we see another major shift, with the soil becoming an N sink as the N inputs to agricultural land increase with the start of more intensive agricultural use, and particularly the use of N fertilizers. For the MRB, this shift can be seen in the period between 1940 and 1960, with soils since that time consistently serving as a net N sink.

For the Susquehanna River Basin, the pattern is quite different, primarily due to the different levels of soil fertility in the SRB compared to the MRB (Figure 7b). In the MRB, median levels of SON, as indicated by National Cooperative Soil Survey (NCSS) soil sampling (NCSS), are currently on the order of 7580 kg ha^{-1} basin wide, or 13,600 kg ha^{-1} in cropland, approximately three to four times those in the SRB (2065 kg ha^{-1} basin wide; 4 600 kg ha^{-1} cropland). The MRB is dominated by mollisols, which are the soils of grassland systems and are characterized by a thick, dark surface horizon; high levels of fertility; and thus high levels of SON [*Kellogg*, 1936; *Post and Mann*, 2005]. In contrast, the SRB is more dominated by inceptisols, which have minimal horizon development, lower levels of fertility, and thus lower levels of SON [*Kellogg*, 1936]. Upon first cultivation the N-poor soils of the SRB would have less N to lose than the N-rich soils of the MRB. Accordingly, although there was a net positive N flux from soils of the SRB from approximately 1800 to 1860, when the conversion of forests to cropland was at its height for the region, these fluxes were relatively small (0.6 ± 0.1 kg ha^{-1}) compared to those for the MRB during this period (1.4 ± 0.6 kg ha^{-1}). Our results show that the SRB then became a net sink for N beginning in the 1890s, although the magnitude of this sink decreased significantly after the 1920s, primarily due to decreases in the percent farmland and a trend toward reforestation. Currently, soil is again serving as a minor N source, with this pattern being attributable to conversion of agricultural land to nonagricultural uses at the same time that atmospheric N deposition is on the decline (Figure 5), thus decreasing the net inputs to the land surface.

One caveat regarding these results is assumptions we have made regarding the potential for N accumulation in nonagricultural soils. Although some research suggests that N is also accumulating in forested [*Fenn et al*., 1998; *De Vries et al*., 2006] and suburban [*Lewis et al*., 2006] areas beyond baseline levels due to both atmospheric N deposition and the use of lawn fertilizers, other work indicates that forested areas in particular may reach a point of N saturation, a condition in which N availability may exceed the capacity of the terrestrial system to further accumulate N [*Aber et al*., 1998; *Gundersen et al*., 1998; *Lovett and Goodale*, 2011; *Niu et al*., 2016]. Due to uncertainty associated with establishment of threshold values for N saturation, we have assumed that no N accumulation would occur beyond levels in the pristine system. In so doing, we likely provide an overly conservative estimate of N retention in soils and thus may overestimate the flux to groundwater.

4.3.3. Groundwater N Accumulation

For both the MRB and SRB, the model results show a net positive flux of N to groundwater storage in response to both new cultivation of land and increases in N surplus values over time (Figure 7), an increase that is consistent with observed increases in groundwater nitrate concentrations at United States Geological Survey sites across the U.S. from 2 mg NO_3^--N mL^{-1} to approximately 15 mg NO_3^--N mL^{-1} between 1940 and 2003 [*Puckett et al*., 2011]. In the MRB, annual model-estimated increases in groundwater N across the watershed were relatively small between 1800 and 1860, averaging 1.2 ± 0.6 kg ha^{-1} and then doubling to 2.8 ± 0.9 kg ha^{-1} during the period of fast land use change between 1860 and 1920. Although annual inputs to groundwater again leveled off to approximately pre-1860 levels after 1920, groundwater in the MRB is currently a N sink, with levels increasing on the order of 3.8 kg ha yr^{-1} (1990–2013).

In the Susquehanna Basin, despite its smaller percentage of agricultural land, the rate of groundwater N accumulation has been consistently greater than that in the MRB, primarily due to the SRB's high atmospheric N deposition rates, nearly twice those in the MRB (23.0 ± 5.4 kg ha^{-1}, SRB; 10.6 ± 1.1 kg ha^{-1}, MRB (1990–2013)). In the nonagricultural areas of the SRB, which make up approximately 80% of the watershed, there is no N removal from crop production and N uptake levels are relatively low [*Baker et al*., 2001; *Lovett and Goodale*, 2011]. With the low-nutrient soils of the region providing little buffering capacity, N from deposition sources passes quickly through the landscape and enter groundwater reservoirs. Such results are also expected based on the higher recharge rates in the SRB (~230 mm yr^{-1}) than the MRB (~125 mm yr^{-1}) [*Wieczorek and LaMotte*, 2010], as *Liao et al*. [2012] have consistently found a strong relationship between mass in groundwater and recharge rate at similar levels of applied N. Currently, the model predicts that increases in groundwater N in the SRB are occurring at a rate of approximately 11.6 kg ha yr^{-1}.

Our results suggest that differences in land use and the high levels of industrial-driven N deposition in the SRB have led to a total N accumulation in the SRB of approximately 980 ± 275 kg ha^{-1}, close to double that in the MRB (508 ± 237 kg ha^{-1}). Although no consistent data are available to estimate or compare actual current magnitudes of nitrate-N in groundwater aquifers between the two watersheds due to the complexity of

the underlying aquifer systems and the large areas covered by the watersheds, concentration data do suggest higher levels for the SRB. In particular, a USGS study of nitrate-N in groundwater of the lower SRB found median nitrate concentrations of 7.3 mg N L^{-1} in agricultural areas of the Piedmont region [*Lindsey et al*., 1997]. In the MRB, USGS National Water-Quality Assessment (NAQWA) data from selected aquifers [*Lindsey and Rupert*, 2012] show median nitrate-N concentrations from 0.9 mg N L^{-1} in alluvial aquifers of Arkansas and Tennessee to 2.5 mg/L in heavily agricultural areas of Iowa and 3.3 mg N L^{-1} in the high plains aquifer in western portions of the MRB. These lower groundwater concentrations for the MRB are consistent with our model prediction of lower N loading to groundwater, as discussed in section 4.3.1.

4.4. Nitrogen Age at the Catchment Outlet

Nitrogen age, which we define herein as the time elapsed from application of N at the land surface to the arrival of N at the catchment outlet, is calculated as a function of (1) watershed travel times and (2) the distribution of N residence times in the soil organic matter pools. We assumed exponential travel time distributions for the hydrologic pathways [*McGuire and McDonnell*, 2006], and our model calibration suggested mean travel times of approximately 16 years (16.0 ± 5.7 years, MRB; 15.6 ± 3.1, SRB) for the two study areas. Although the estimation of travel times through subsurface pathways is notoriously complex, particularly in varied geologic settings [*Phillips et al*., 1999], our modeled results are in line with literature reports. In particular, in subwatersheds within the SRB and MRB, travel times have been found to range from less than a year to more than 50 years [*Phillips et al*., 1999; *Lindsey et al*., 2003; *Schilling et al*., 2007; *Sanford and Pope*, 2013].

As discussed in section 2.2.2, isotope studies suggest that the majority of nitrate-N leaching from the soil profile has passed through the soil organic N pool [*Haag and Kaupenjohann*, 2001; *Spoelstra et al*., 2001]. Accordingly, N residence times within the soil profile, which are controlled by organic N mineralization rates, can be considered to represent a significant fraction of the time lag between N application on land and arrival at the catchment outlet. Organic matter in soil is mineralized to more mobile inorganic forms on timescales ranging from days to millennia [*Jenkinson*, 1990; *Torn et al*., 1997; *Gleixner et al*., 2002]. Within our modeling framework, residence times in soil organic matter are dependent on whether N is in the active pool or the protected pool. Based on our calibration results, the mean residence times of SON in the active pools for the two watersheds are less than 10 years (8.8 years, MRB; 7.6 years, SRB). For the protected pool, however, these times are 2 orders of magnitude greater (4280 years, MRB; 1636 years, SRB).

Based on the above, we found the N load at the catchment outlet in both of the study watersheds to be dominated by legacy N (Figure 8). For the MRB, we again see the strong signature of the plowing of pristine lands in the late eighteenth and early nineteenth centuries. During this period, previously protected soil organic N, with its very long residence times, was exposed to the stresses of climate and mechanical disruption, leading to rapid mineralization of older SON [*Davidson and Ackerman*, 1993; *Six et al*., 2002]. For the period between 1860 and 1920, more than 60% of the N flux at the MRB outlet would have entered the terrestrial system more than 50 years ago, with much of it originating from biological N fixation during the presettlement period. Currently, legacy N in the MRB accounts for approximately 85% of all the annual N load, with more than half of that 85% having originated from anthropogenic sources since 1960. For the SRB, 47% of the current load can be attributed to legacy sources, with the rest being attributed to current year N surplus. Nearly all of the annual legacy N loading ($>$95%) is anthropogenic in origin, having been introduced into the terrestrial system since 1960.

4.5. Characterization of Nitrogen Sources at the Catchment Outlet

As more aggressive nutrient reduction goals are being set for both Mississippi and Chesapeake Bay watersheds, much attention has focused on the implementation of new management practices and conservation measures [*Rabotyagov et al*., 2010; *Reckhow et al*., 2011]. To effectively meet such goals, it is crucial to understand the primary sources of nutrients reaching the catchment outlet. For both the MRB and SRB, changes in land use and management have led to changes over time in the relative importance of the different sources of N (Figure 9). As seen in the figure, the major change for the MRB has come with the use of N fertilizer, which now accounts for approximately 28% of total N loading. Although the use of commercial N fertilizer began in earnest in the 1940s, our results show that it took nearly two decades for fertilizer to make a significant contribution to N loading. More specifically, fertilizer N accounted for a negligible portion of N loads in the 1940s;

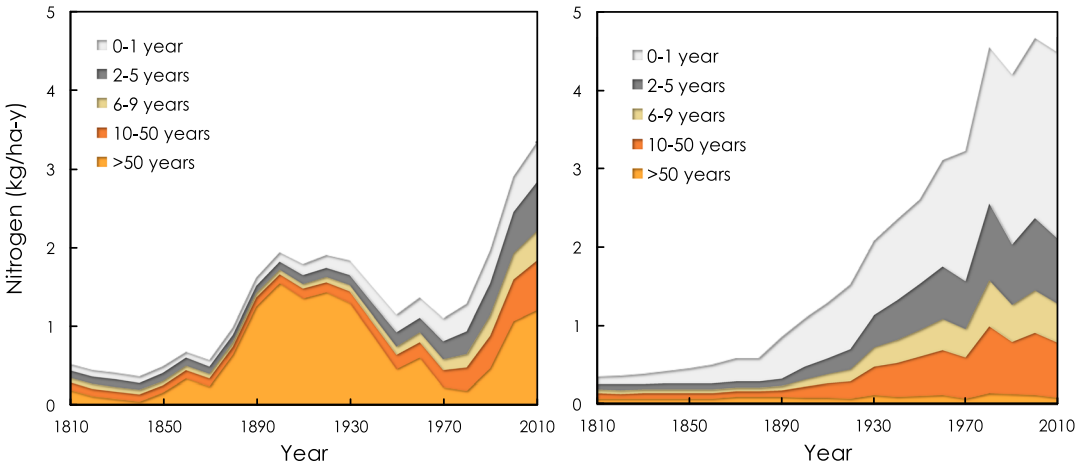

Figure 8. Age of nitrogen at the catchment outlet. The figure shows changes in the distribution of N age over the study period, by decade, for the Mississippi (left) and Susquehanna (right) River Basins.

this percentage had increased to approximately 5% by the 1960s, then growing to 18% in the 1970s to 28% now.

In contrast, although N fertilizer use also saw a more than 100-fold increase between the 1950s and the present day in the SRB, fertilizer N makes up a much smaller portion of the N-loading budget, accounting for only 4% of total loads. Instead, N loading in the SRB has come to be dominated by atmospheric N deposition. In the 1950s, the relative importance of atmospheric deposition was comparable between the two basins (31% of N loading, MRB; 34%, SRB). However, due to urbanization and increased fossil fuel use as well as the density of livestock operations [*Reckhow et al*., 2011] in the SRB, atmospheric N deposition continued to increase into the 1990s, accounting for as much as 350 kt of annual N loading. The greater importance of N deposition in the SRB is also a result of the relatively smaller proportion of agricultural land in the watershed, which means that atmospheric N deposition is the only anthropogenic N input across approximately 85% of the watershed. Although atmospheric N deposition rates have begun to show a significant downward trend in the northeastern U.S. [*Houlton et al*., 2013], N deposition continues to account for approximately 40% of N loading in the SRB.

Manure N also constitutes a large fraction of annual N loading in the SRB (27%). Throughout the Chesapeake Bay region, not only is the density of livestock production relatively high, the small proportion of agricultural land leads to a lack of a local land base for spreading livestock manure [*Guan and Holley*, 2011]. Accordingly,

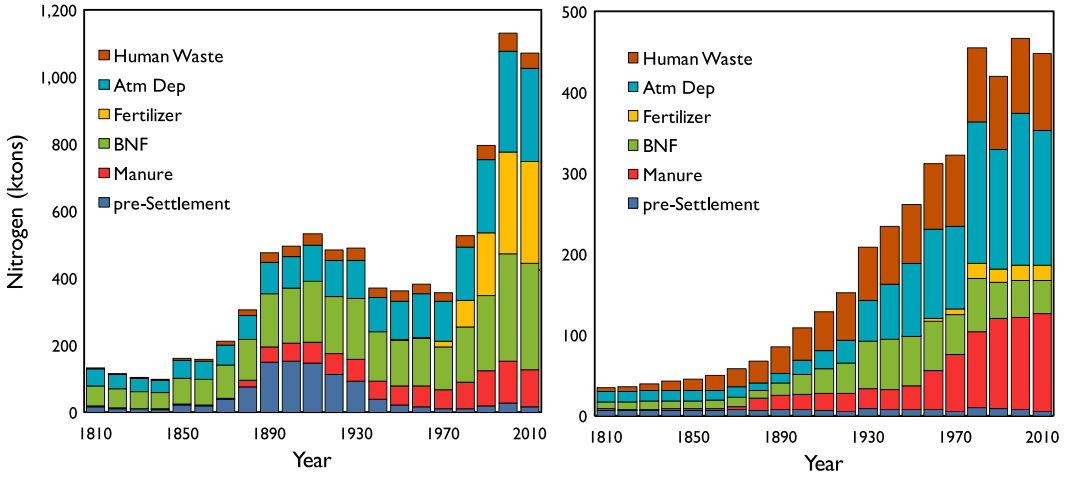

Figure 9. Sources of nitrogen at the catchment outlet. The figure shows changes in the distribution of N age over the study period by decade.

there are higher per area inputs of manure to agricultural land throughout the SRB, leading to oversaturation of land with surplus liquids and nutrients and higher levels of N runoff. Interestingly, for the MRB, although the magnitude of manure production has increased more than fivefold over the study period, it makes up only 10% of total N loading, a much lower proportion than in the SRB. It should be noted here, however, that approximately half of the atmospheric N deposition in both watersheds can be traced back to volatilization of a combination of fertilizer and animals waste [*Hong et al*., 2011; *Schindler* 2006]. In addition, a large portion of U.S. cropland is devoted to producing animal feed, e.g., more than 40% of corn and 80% of soybeans (USDA and Economic Research Service), meaning that livestock make a bigger contribution to watershed N loading than may be suggested by manure N production alone.

As a caveat, it should be noted that fundamental assumptions for the modeling framework do contribute to some uncertainty in the source apportionment, as represented in Figure 9. In particular, as a simplifying feature of the model, denitrification rate constants are effective, watershed-scale rate constants, with N removal in surface water being lumped together with removal in other compartments such as groundwater and wastewater treatment plants. Accordingly, though the model does take into account the overall magnitude of denitrification, including that occurring in surface water, it does not provide a full representation of the spatial dynamics of watershed retention processes. Such a simplification may particularly impact our calculation of wastewater N inputs to the watershed, as the amount of in-stream retention of wastewater N may have a strong dependence on where it is released into the stream network, with more retention occurring when the release occurs at upstream locations. Interestingly, however, our calibrated values suggest an 83% retention of wastewater N for both the MRB and SRB, which is well in line with a previous estimate of 80% wastewater N retention for 153 watersheds of the MRB [*David et al*., 2010].

5. Implications and Significance

In 2008, the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force released an "action plan" to reduce the size of the Gulf of Mexico's summer hypoxic zone to less than 5000 km^2 by 2015 [*USEPA*, 2008; *Rabotyagov et al*., 2010]. With the 2014 and 2015 dead zones being measured at 2 to 3 times the targeted size (13,085 km^2 and 16,768 km^2, respectively [*NOAA*, 2015]), the deadline for achieving this goal has now been extended to 2035. Similarly, the Chesapeake Bay Program a broad partnership among multiple states and the U.S. Environmental Protection Agency, committed in 1987 to reducing "controllable" N and P loading to the Chesapeake Bay by 40% by the year 2000. A 2011 report evaluating the success of these efforts notes that progress has been limited and that the nutrient reduction goals have still not been attained [*Reckhow et al*., 2011].

Such delays in achieving reduction goals can be attributed to a number of causes, from institutional inertia [*Berkes et al*., 2008], to a lack of funding for needed interventions [*USDA*, 2015], and to evolving knowledge regarding the effectiveness of specific intervention strategies [*Mitsch et al*., 2001; *Bouraoui and Grizzetti*, 2014]. Increasingly, however, policymakers and researchers alike have pointed to the existence of legacy nutrients in human-impacted catchments as a cause for time lags in catchment response [*Meals et al*., 2010; *Haygarth et al*., 2014; *Van Meter and Basu*, 2015; *Worrall et al*., 2015; *Van Meter et al*., 2016], time lags that present obvious challenges to meeting current nutrient reduction goals. Despite this growing recognition of the need for considering landscape-scale nutrient legacies when setting policy goals and implementing remediation strategies, there remains a lack of appropriate models that can capture land use change and water quality impacts over long time scales. In the present study, we have taken a long-term approach to exploring the possible impacts of legacy-related time lags within the MRB and SRB, pairing more than two centuries of watershed-scale N input data with the ELEMeNT modeling framework in order to more adequately take into account the development of legacy N stores within these watersheds and to quantify the role that these legacies play in multidecadal trajectories of N loading.

Our results first show sevenfold and fourteenfold increases in N loading for the MRB and SRB, respectively, since preindustrial times. Although such increases are clearly linked to twentieth century increases in the use of commercial N fertilizers, N loading has also at times shown a decoupling from N inputs due to the influence of legacy N. For the MRB, this decoupling occurred most prominently with the release of large landscape-scale N legacies during the period of European settlement; for the SRB, however, it is most clearly seen as a function of more recent anthropogenic legacies in the SRB, as N surplus values have decreased,

while N loading has remained elevated (Figure 6). The model results also demonstrate the development of large subsurface N legacies for both of the study watersheds, although the magnitudes and locations of the accumulation differ between the two watersheds. In particular, the lower-fertility soil of the SRB together with higher annual runoff leads to less N accumulation in soil but greater groundwater accumulation and higher levels of stream N loading compared to MRB.

Our results indicate that current annual N loading in both the MRB and SRB is strongly impacted by legacy sources, which, as described in 3.4, we define as N greater than 1 years of age (85%, MRB; 47%, SRB). Accordingly, to achieve both short-term and long-term success in reducing N loads to coastal areas, it may be necessary to take a two-pronged approach to nutrient management in these watersheds. For the fastest reductions in loading, it will be important to target current year sources. For the MRB, which is the more legacy-driven system and thus more bound by inertia, short-term gains will be more difficult to achieve. In this case, a targeted short-term approach like the increased use of constructed wetlands to intercept runoff from tile drains and flooding streams [*Mitsch et al*., 2001] would need to be integrated with longer-term approaches of reductions in N application rates and modification of tile drainage networks to slow the transport of N to nearby waterbodies [*Kröger et al*., 2012; *Drury et al*., 2014]. In the SRB, where both animal manure and urban wastewater represent significant current year sources, upgrades to wastewater treatment plants (WWTPs) [*Carey and Migliaccio*, 2009; *Zimmerman and Dooley*, 2014] and more innovative forms of manure management, including the development of biogas reactors for both waste treatment and energy production [*Weiland*, 2006], may have a larger short-term impact. Indeed, WWTP upgrades have accounted for a significant portion of nutrient reductions already achieved in the Chesapeake Bay region [*Reckhow et al*., 2011], and the wastewater treatment plant at Harrisburg, Pennsylvania, the largest point source of nitrogen to the Susquehanna River, is currently undergoing a major upgrade scheduled for completion in 2016 [*Capital Region Water*, 2016].

For the remediation of legacy N sources, riparian buffers and wetlands, in areas where a significant portion of groundwater intersects the buffered area, may represent the best approach to preventing groundwater N from entering waterways [*Messer et al*., 2012]. Although soil N legacies can serve as a long-term source to groundwater, opportunities may also be available to effectively utilize the legacy N through the planting of cover crops [*Drury et al*., 2014; *Malone et al*., 2014] or by the conversion of areas currently in row crop to perennial vegetation, including biofuel crops such as switchgrass or Miscanthus [*Costello et al*., 2009; *Wu and Liu*, 2012].

The most important finding of the current study is that significant legacies of N have accumulated within the Mississippi and Susquehanna River Basins. Moreover, plentiful evidence exists to suggest that these two heavily impacted watersheds are not unique and that legacy nutrient stores likely play a dominant role throughout the world in controlling nutrient loading to coastal areas [*Sharpley et al*., 2013; *Haygarth et al*., 2014; *Withers et al*., 2014; *Powers et al*., 2016]. As more stringent nutrient control measures continue to be put into place [*Council of European Communities*, 2000; *USEPA*, 2008; *Backer et al*., 2010; *Reckhow et al*., 2011], our work underlines the necessity for further exploring the magnitudes and spatial distribution of legacy nutrient stores so as to better our ability to meet nutrient reduction goals and to reduce uncertainties regarding the timescales over which legacy nutrients will adversely affect water quality.

Acknowledgments
The present work was financially supported by an NSERC Discovery Grant and by an Ontario Early Researcher Award, both awarded to N.B. Basu. Agricultural census and survey data were retrieved online from https://www.agcensus.usda.gov Atmospheric deposition data were retrieved online from http://nadp.sws.uiuc.edu/data/ntn/ and from https://daac.ornl.gov/CLIMATE/guides/global_N_deposition_maps.html USGS water quality data were retrieved from http://waterdata.usgs.gov/nwis/qw.

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